INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: PREPARING A HIGH VISCOSITY INDEX, LOW BRANCH INDEX DEWAXED OIL

(57) Abstract

An integrated process for preparing a lubricating oil base stock includes an isomerization step followed by a solvent dewaxing step. A waxy feed is isomerized to an intermediate pour point, which is at least 6 °C above a target pour point, over a select molecular sieve having specified pore properties. The isomerized oil is then solvent dewaxed to a very low pour point. This process produces a dewaxed lubricating oil base stock which has an exceptionally high viscosity index.

1           **PREPARING A HIGH VISCOSITY INDEX,**

2           **LOW BRANCH INDEX DEWAXED OIL**

3           This patent application claims priority from U.S. Provisional Patent

4    Application Serial No. 60/077070, filed March 6, 1998, the specification of

5    which is incorporated herein by reference for all purposes.

6                    <u>BACKGROUND OF THE INVENTION</u>

7

8           The present process is a dewaxing process for producing very high

9    viscosity index, low pour point lubricating oil base stocks from a mineral oil

10   feed. When preparing a lubricating oil base stock from a mineral oil, viscosity

11   index is generally increased to a target value during an upgrading step using

12   hydrocracking, solvent refining, etc. Pour point is generally reduced to a

13   target value during a dewaxing step, using catalytic or solvent dewaxing. In

14   conventional processes, the viscosity index generally decreases during

15   dewaxing, since conventional dewaxing processes remove high viscosity

16   index wax from the lubricating oil base stock. Improvements in automotive

17   engine design is putting ever increasing pressure on the quality of motor oils.

18   Demand for low volatility oils having superior low temperature properties is

19   increasing, and refiners are constantly looking for new processes to aid them

20   in meeting current demands.

21          High quality lubricants should be, and generally are, paraffinic in

22   nature, since paraffins have a high viscosity index. However, normal

23   paraffins, in particular, are waxy in character, and contribute to a high pour

24   point in the oil. Conventional processes for removing these normal paraffins

25   reduce yield of the lubricant, and have a tendency to reduce the viscosity

26   index of the dewaxed oil. The viscosity index may be increased in the

27   lubricating oil base stock by addition of viscosity index improvers. However,

28   viscosity index improvers are expensive, and tend to fragment at conditions of

29   high temperature and high shear, both of which are commonly found in

30   modern automotive engines.

1        Synthetic lubricants may be used when very low pour point and very

2   high viscosity index lubricants are desired. But the starting materials used to

3   make the synthetic lubricants, and the processes used in manufacturing these

4   lubricants, are very expensive. The need remains for a lubricating oil base

5   stock, having synthetic-like properties but prepared from a mineral oil feed

6   using methods which are similar to those presently employed in refinery

7   processes.

8        A major breakthrough came with the discovery of new dewaxing

9   catalysts which were found to isomerize rather than crack the wax molecules.

10   Isomerization alters the molecular structure of wax molecules, and generally

11   decreases the pour point of the molecule without significantly changing its

12   boiling point. In contrast to solvent dewaxing and to wax cracking, isomerized

13   molecules are retained in the lubricating oil base stock, increasing yield of

14   lubricating oil base stock without reducing viscosity index significantly . A

15   particularly important group of isomerization catalysts include the

16   silicoaluminophosphate molecular sieves (SAPO). The preparation of

17   silicoaluminophosphate molecular sieves, including SAPO-11, SAPO-31 and

18   SAPO-41, are taught, for example, in U.S. Patent No. 4,440,871. Dewaxing

19   processes using such molecular sieves are taught in U.S. Patent

20   No. 4,859,311; U.S. Patent No. 4,867,862; U.S. Patent No. 4,921,594; U.S.

21   Patent No. 5,082,986; U.S. Patent No. 5,135,638; U.S. Patent No. 5,149,421;

22   U.S. Patent No. 5,246,566; U.S. Patent No. 5,413,695; and U.S. Patent

23   No. 4,960,504.

24        SAPO molecular sieves belong to an important class of non-zeolitic

25   molecular sieve dewaxing catalysts which are useful as isomerization

26   catalysts for converting wax and wax-like components. Non-zeolitic molecular

27   sieves are microporous compositions that are formed from $AlO_2$ and $PO_2$

28   tetrahedra which form 3-dimensional crystalline structures, and are described

29   broadly for this use in U.S. Patent No. 4,906,351 and U.S. Patent

30   No. 4,880,760.

1       These catalysts with isomerization and hydroisomerization activity have

2   been found to provide a method for preparing very high viscosity index

3   lubricating oil base stocks from waxy feedstocks in a single reaction step.

4   Producing a $C_{20}{}^{+}$ lube oil from olefins, including normal alpha olefins, using an

5   intermediate pore size molecular sieve and at least one Group VIII metal, is

6   taught in U.S. Patent No. 5,082,986. In U.S. Patent No. 5,135,638, a waxy

7   feed containing greater than about 50% wax is isomerized over a catalyst

8   comprising a molecular sieve having 1-D pores having a minor axis between

9   about 4.2Å and about 4.8Å and a major axis between about 5.4Å and about

10   7.0Å and at least one Group VIII metal at a pressure of from about 15 psig

11   (103 kPa) to about 2000 psig (13.8 MPa). SAPO-11, SAPO-31, SAPO-41,

12   ZSM-22, ZSM-23 and ZSM-35 are included in U.S. Patent No. 5,135,638 as

13   intermediate pore size materials which possess the indicated pore geometry.

14   In U.S. Patent No. 5,282,958, a feed including straight chain and slightly

15   branched chain paraffins having 10 or more carbon atoms is isomerized with

16   an intermediate pore size molecular sieve having a defined pore geometry,

17   crystallite size, acidity and isomerization selectivity. Feeds which may be

18   processed by the method of U.S. Patent No. 5,282,958 include waxy feeds,

19   which contain greater than about 50% wax. Such feeds are also taught as

20   often containing greater then 70% paraffinic carbon. U.S. Patent

21   No. 5,376,260 is directed to pour point reduction of a heavy oil which contains

22   naphthenic wax, using SSZ-32. Heavy oils comprising up to 100% wax are

23   taught.

24       Large pore zeolites represent another class of catalysts which have

25   been taught for wax isomerization. EP 464546 teaches producing a high

26   viscosity index lubricant from a petroleum wax feed having a paraffin content

27   of at least 40 weight percent. The catalyst is a low acidity zeolite

28   isomerization catalyst having an alpha value of not more than 20. Zeolite

29   beta which contains boron as a framework component of the zeolite is taught

30   as being preferred. The catalyst in WO 96/26993 is a low acidity large pore

31   zeolite isomerization catalyst having a ratio of $SiO_2/Al_2O_3$, as synthesized, of

1   at least 200:1. WO 96/13563 teaches an isomerization process for producing

2   a high viscosity index lubricant using a low acidity large pore molecular sieve

3   having a crystal size of less than 0.1 micron, an alpha value of not more than

4   30 and containing a noble metal hydrogenation component. EP 225053

5   teaches isomerization dewaxing using a large pore, high silica zeolite

6   dewaxing catalyst, followed by a subsequent dewaxing step which selectively

7   removes the more waxy n-paraffin components. The selective dewaxing step

8   may be either a solvent or a catalyst dewaxing, preferably using highly shape

9   selective zeolite such as ZSM-22 or ZSM-23.

10   While the intermediate pore size molecular sieves have been shown to

11   be effective for producing high viscosity index lubricating oil base stocks, the

12   need remains for even higher viscosity index products which have been

13   dewaxed to a low pour point.

14   ## SUMMARY OF THE INVENTION

15   An object of the present invention is to provide a process for producing an oil,

16   having a very high viscosity index and a very low pour point, which is suitable

17   for use as a lubricating oil base stock. The feedstock to the present process

18   is a waxy feed which may be derived from mineral oils and mineral oil crudes.

19   The oil which is produced has lubricating oil properties that approach, and

20   may exceed, the lubricating oil properties of a synthetic lubricating oil base

21   stock. Accordingly, the present invention provides a process for preparing an

22   oil suitable for use as a lubricating oil base stock and having a viscosity index

23   of greater than 140 and a target pour point of less than or equal to −10°C

24   comprising:

25   a)  contacting a waxy feed over a catalyst comprising a molecular sieve

26        having 1-D pores with a pore diameter of between about 5.0 Å and

27        about 7.0 Å, and at least one Group VIII metal, at a pressure of from

28        about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an

29        isomerized oil having a pour point of at least 6°C above a target pour

30        point; and

1       b) solvent dewaxing the isomerized oil to produce a lubricating oil base

2           stock having the target pour point and a viscosity index of greater than

3           about 140.

4       A particularly preferred molecular sieve useful in the isomerization step

5   has sufficient isomerization selectivity such that, when contacting a n-$C_{24}$ feed

6   at a total pressure of 1000 psig (6.99 MPa), hydrogen flow equivalent to 6.7

7   MSCF/bbl (1010 std liters $H_2$/kg oil), and a feed rate equivalent to 0.6 $hr^{-1}$

8   LHSV with a catalyst comprising the molecular sieve, to produce a 316°C+

9   dewaxed product having a pour point of about +20°C and solvent dewaxing

10  the dewaxed product to a pour point of –15°C or below, an isomerized

11  product having a branching index of less than about 1.75 is formed.

12      The process is capable of producing an oil having a very high viscosity

13  index, e.g., greater than about 140 or even greater than about 150.  The

14  process is further capable of producing an oil having a very low pour point,

15  e.g. less than or equal to about -10°C, or less than or equal to about -20°C, or

16  even less than or equal to about -30°C.

17      In another embodiment, the present invention provides a unique

18  lubricating oil base stock, which has a viscosity index of at least about 140,

19  preferably at least about 150 and more preferably at least about 160, a pour

20  point of less than or equal to about -10°C, and a viscosity, measured at

21  100°C, of about 3 cSt or less.

22                          IN THE FIGURES

23      Figure 1 shows the benefit of isomerizing a waxy feed with SM-3 and

24  solvent dewaxing the isomerized oil compared to isomerizing the waxy feed

25  alone.

26      Figure 2 shows the benefit of isomerizing a waxy feed with SSZ-32 and

27  solvent dewaxing the isomerized oil compared to isomerizing the waxy feed

28  alone.

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## DETAILED DESCRIPTION OF THE INVENTION

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3    Normal paraffins are a major contributor to wax and a high pour point

4    in a lubricating oil base stock. It is desirable to isomerize the normal paraffins

5    to low pour point branched paraffins which retain the boiling range of the

6    normal paraffins from which there were converted.

7    Among other factors, the present invention is based on the discovery

8    that the number of branches produced while isomerizing a normal paraffin

9    molecule significantly impacts the quality of the dewaxed oil product. For

10    example, isomerizing a normal $C_{24}$ paraffin, tetracosane, using a large pore

11    zeolite catalyst conventionally taught for wax isomerization, generally

12    produces a significant quantity of triply branched paraffin isomers. Even

13    medium pore catalysts taught for wax isomerization, when isomerizing a waxy

14    feed to a low pour point, produces significant quantities of the triply branched

15    isomers. While not wishing to be bound by theory, it is believed that normal

16    paraffins are first converted during wax isomerization to a singly branched

17    paraffin having a methyl ($-CH_3$) or ethyl ($-C_2H_5$), branch near the end of the

18    paraffin backbone. Additional isomerization reactions move the branch

19    toward the center of the paraffin molecule and/or add a second branch to the

20    paraffin molecule. Each of these two isomerization reaction steps reduces

21    pour point.

22    However, conventional single stage and/or large pore zeolite dewaxing

23    processes are unselective for forming branches. These unselective catalysts

24    produce triply (or even more highly) branched isomers along with the singly

25    and doubly branched isomers before reaching the target pour point. These

26    highly branched molecules have an increased tendency to crack and have a

27    lower viscosity index than do singly or doubly branched paraffins.

28    Furthermore, the addition of a third branch to a doubly branched paraffin

29    often results in relatively little additional pour point reduction. Thus, these

30    conventional processes are prevented from producing lubes with the desired

31    viscosity index and pour point properties.

1        In the present process, normal paraffins are isomerized at high

2      selectivity to singly and doubly branched paraffins using a process which

3      produces few triply branched paraffins. The shape selective catalyst of the

4      present invention, comprising a 1-D intermediate pore size molecular sieve,

5      restricts the amount of triply branched paraffins which are formed in the

6      isomerization of a waxy feed, while producing a product having an

7      intermediate pour point. The remaining wax is removed in a solvent dewaxing

8      step to produce a lubricating oil base stock with a very low pour point and a

9      viscosity index which approaches, and can exceed, the viscosity index of

10     synthetic lubricants having the same viscosity.

11     As used herein, a normal paraffin, or alkane, is a saturated aliphatic

12     hydrocarbon containing only $-CH_3$ and $-CH_2-$ groups. A branched paraffin is

13     a saturated aliphatic hydrocarbon containing one or more

$$\overset{\displaystyle R}{\underset{\displaystyle}{R_1\overset{|}{C}HR_2}}$$

or

$$\underset{\displaystyle R}{\overset{\displaystyle R}{R_1\overset{|}{\underset{|}{C}}R_2}}$$
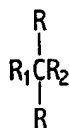
14     groups. As used herein, each R represents a branch, where R is an alkyl

15     independently selected from $-CH_3$, $-C_2H_5$, $-C_3H_7$, or $-C_4H_9$, and preferably

16     from $-CH_3$ or $-C_2H_5$. $R_1$ and $R_2$ represent portions of the paraffin chain or

17     backbone. Thus, a singly branched paraffin has one R group per paraffin

18     molecule, a doubly branched paraffin two R groups, a triply branched paraffin

19     three R groups, etc.

20        The feedstock to the present process is a "waxy feed". The feedstock

21     will normally be a $C_{20}^+$ feedstock, generally boiling above about 316°C and

22     containing paraffins, olefins, naphthenes, aromatics and heterocyclic

23     compounds and a substantial proportion of higher molecular weight

1    n-paraffins and slightly branched paraffins which contribute to the waxy

2    nature of the feedstock. Hydroprocessed stocks are a convenient source of

3    stocks of this kind and also of other distillate fractions since they normally

4    contain significant amounts of waxy n-paraffins.

5    As used herein, the term "waxy feed" includes petroleum waxes.

6    Exemplary suitable feeds for use in the process of the invention also include

7    waxy distillate stocks such as gas oils, lubricating oil stocks, synthetic oils and

8    waxes such as those by Fischer-Tropsch synthesis, high pour point

9    polyalphaolefins, foots oils, normal alpha olefin waxes, slack waxes, deoiled

10   waxes and microcrystalline waxes. Slack wax is wax recovered from a

11   conventional solvent dewaxing process. Slack wax can be obtained from

12   either a straight run gas oil, a hydrocracked lube oil or a solvent refined lube

13   oil. Hydrocracking is preferred because that process can also reduce the

14   nitrogen content to low values. With slack wax derived from solvent refined

15   oils, deoiling can be used to reduce the nitrogen content. Optionally,

16   hydrotreating of the slack wax can be carried out to lower the nitrogen content

17   thereof. Slack waxes possess a very high viscosity index, normally in the

18   range of from 120 to 200, depending on the oil content and the starting

19   material from which the wax has been prepared. Slack waxes are therefore

20   eminently suitable for the preparation of lubricating oils having very high

21   viscosity indices, i.e., from about 140 to about 180. Foots oil is prepared by

22   separating oil from the wax. The isolated oil is referred to as foots oil.

23   The feedstock employed in the process of the invention preferably

24   contains greater than about 50% wax, more preferably greater than about

25   80% wax, most preferably greater than about 90% wax. However, a highly

26   paraffinic feed having a high pour point, generally above about 0°C, more

27   usually above about 10°C, but containing less than 50% wax is also suitable

28   for use in the process of the invention. Such a feed should preferably contain

29   greater than about 70% paraffinic carbon, more preferably greater than about

30   80% paraffinic carbon, most preferably greater than about 90% paraffinic

31   carbon.

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1       A catalyst useful in the present process comprises an intermediate

2   pore size molecular size and a hydrogenation component. Catalysts of this

3   type are taught in U.S. Patent No. 5,135,638, the entire disclosure of which is

4   incorporated herein by reference for all purposes. The phrase "intermediate

5   pore size", as used herein means an effective pore aperture in the range of

6   from about 5.0 to about 7.0 Å, preferably from about 5.3 to about 6.5Å, when

7   the porous inorganic oxide is in the calcined form. The effective pore size of

8   the molecular sieves can be measured using standard adsorption techniques

9   and hydrocarbonaceous compounds of known minimum kinetic diameters.

10   See Breck, Zeolite Molecular Sieves. 1974 (especially Chapter 8); Anderson

11   et al., J. Catalysis 58, 114 (1979); and U.S. Pat. No. 4,440,871, the pertinent

12   portions of which are incorporated herein by reference.

13       In performing adsorption measurements to determine pore size,

14   standard techniques are used. It is convenient to consider a particular

15   molecule as excluded if it does not reach at least 95% of its equilibrium

16   adsorption value on the molecular sieve in less than about 10 minutes

17   (p/po=0.5; 25°C).

18       Intermediate pore size molecular sieves will typically admit molecules

19   having kinetic diameters of 5.3 to 6.5Å with little hindrance. Examples of such

20   compounds (and their kinetic diameters in Å) are: n-hexane (4.3),

21   3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds

22   having kinetic diameters of about 6 to 6.5Å can be admitted into the pores,

23   depending on the particular sieve, but do not penetrate as quickly and in

24   some cases are effectively excluded. Compounds having kinetic diameters in

25   the range of 6 to 6.5Å include: cyclohexane (6.0), 2,3-dimethylbutane (6.1),

26   and m-xylene (6.1). Generally, compounds having kinetic diameters of

27   greater than about 6.5Å do not penetrate the pore apertures and thus are not

28   absorbed into the interior of the molecular sieve lattice. Examples of such

29   larger compounds include: o-xylene (6.8), 1,3,5-trimethylbenzene (7.5), and

30   tributylamine (8.1). While the effective pore size as discussed above is

31   important to the practice of the invention, not all intermediate pore size

1    molecular sieves having such effective pore sizes are advantageously usable

2    in the practice of the present invention. Indeed, it is essential that the

3    intermediate pore size molecular sieve catalysts used in the practice of the

4    present invention have a very specific pore shape and size as measured by

5    X-ray crystallography. First, the intracrystalline channels must be parallel and

6    must not be interconnected. Such channels are conventionally referred to as

7    1-D diffusion types or more shortly as 1-D pores. The classification of

8    intrazeolite channels as 1-D, 2-D and 3-D is set forth by R. M. Barrer in

9    Zeolites, Science and Technology, edited by F. R. Rodrigues, L. D. Rollman

10   and C. Naccache, NATO ASI Series, 1984 which classification is

11   incorporated in its entirety by reference (see particularly page 75). Known

12   1-D zeolites include cancrinite hydrate, laumontite, mazzite, mordenite and

13   zeolite L.

14          In general, the pores of the molecular sieve have a major axis between

15   about 5.0 Å and about 7.0 Å, i.e. the pore diameter of the molecular sieve is

16   between about 5.0 Å and about 7.0 Å. In one embodiment, the preferred

17   molecular sieves useful in the practice of the present invention have pores

18   which are oval in shape, by which is meant the pores exhibit two unequal

19   axes referred to herein as a minor axis and a major axis. The term oval as

20   used herein is not meant to require a specific oval or elliptical shape but

21   rather to refer to the pores exhibiting two unequal axes. In particular, the 1-D

22   pores of the preferred molecular sieves useful in the practice of the present

23   invention have a minor axis between about 3.9Å and about 4.8Å and a major

24   axis between about 5.4Å and about 7.0Å as determined by conventional

25   X-ray crystallography measurements, following the measurement convention

26   of W. M. Meier and D. H. Olson, *ATLAS OF ZEOLITE STRUCTURE TYPES,*

27   Butterworth-Heinemann, Third Revised Edition, 1992.

28          The present invention makes use of molecular sieve catalysts with

29   selected shape selectivity properties. These shape selectivity properties are

30   defined by carrying out standard isomerization selectivity tests for isomerizing

31   tetracosane (n-$C_{24}$). The test conditions include a total pressure of 1000 psig

1   (6.89 MPa), hydrogen flow equivalent to 6.7 MSCF/bbl (1010 std liters $H_2$/kg

2   oil), a feed rate equivalent to 0.6 $hr^{-1}$·LHSV and the use of 0.5g of catalyst

3   (impregnated with 0.5 wt% Pt and sized to 24-42 mesh [0.35 mm – 0.70 mm])

4   loaded in the center of a 3 feet long (0.91 m) by 3/16 inch (0.48 cm) inner

5   diameter stainless steel reactor tube (the catalyst is located centrally of the

6   tube and extends about 1 to 2 inches [2.54-5.08 cm] in length) with alundum

7   loaded upstream of the catalyst for preheating the feed. The reactor

8   temperature is adjusted to achieve a pour point of about +20°C in the 600°F+

9   (316°C) distillation bottoms of the reactor effluent. The 600°F+ (316°C)

10  distillation bottoms are then solvent dewaxed to a pour point of about –15°C.

11      To account for the extent of isomerization, a branching index is defined

12  to characterize the average number of branches per $C_{24}$ molecule.

13  $$BranchingIndex = \sum_i i * b_i \Big/ b_t$$

14      where $b_i$ is the amount of paraffins in the product with an "i" number of

15  branches, and $b_t$ is the total amount of paraffins in the product (both normal

16  and branched).

17      The branching index is determined by analyzing a sample of the

18  product from the standard isomerization selectivity test using carbon-13 NMR

19  according to the following four-step process. References cited in the

20· description detail the process steps.

21      1. Identify the CH branch centers and the $CH_3$ branch termination points

22          using the DEPT Pulse sequence (Doddrell, D.T.; Pegg, D. T.; Bendall,

23          M.R. *J. Magn. Reson.* **1982**, 48, 323ff.).

24      2. Verify the absence of carbons initiating multiple branches (quaternary

25          carbons) using the APT pulse sequence (Patt, S.L.; Shoolery, J. N. *J.*

26          *Magn. Reson.* **1982**, 46, 535ff.)

27      3. Assign the various branch carbon resonances to specific branch

28          positions and lengths using tabulated and calculated values

1     (Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **43**, 1971 1245ff: Netzel,

2     D.A. *et.al. Fuel,* **60**, 1981, 307ff.

3     4. Quantify the relative frequency of branch occurrence by comparing the

4     integrated intensity of its terminal methyl carbon to the intensity of a

5     single carbon (=total integral/number of carbons per molecule in the

6     mixture). For the unique case of the isopropyl branch, where both

7     methyl occur at the same resonance position, the intensity was divided

8     by two before doing the frequency of branch occurrence calculation.

9     All measurements were performed with Varian 300 MHz spectrometers.

10     In all cases the spectral width was limited to the saturated carbon region,

11     about 0-80 ppm vs. TMS (tetramethyl silane). 15-25% solutions by weight in

12     chloroform-d1 excited by 45° pulses followed by an 0.8 sec acquisition time.

13     In order to minimize non uniform intensity data, the proton decoupler was

14     gated off during a 10 sec delay prior to the excitation pulse and on during

15     acquisition. Total experiment times ranged from 11-80 minutes. The DEPT

16     and APT sequences were carried out according to literature descriptions with

17     minor deviations described in the Varian operating manuals.

18     A catalyst, if it is to qualify as a catalyst of this invention, when tested in

19     this manner, must convert sufficient normal $C_{24}$ paraffin to form an isomerized

20     product having a pour point of about –15°C or less and a branching index of

21     less than about 1.75. Non-zeolitic molecular sieves having the characteristics

22     of an intermediate pore size molecular sieve as described herein are useful in

23     the present process. Non-zeolitic molecular sieves are microporous

24     compositions that are formed from $AlO_2$ and $PO_2$ tetrahedra. Thus, the

25     process of the invention may be carried out using a catalyst comprising an

26     intermediate pore size non-zeolitic molecular sieve and at least one

27     Group VIII metal. Non-zeolitic molecular sieves are described, for example,

28     in U.S. Patent No. 4,861,743, the disclosure of which is completely

29     incorporated herein by reference for all purposes. Non-zeolitic molecular

30     sieves include aluminophosphates ($AlPO_4$) as described in U.S. Patent

31     No. 4,310,440, silicoaluminophosphates (SAPO), metalloaluminophosphates

1    (MeAPO), and nonmetal substituted aluminophosphates (ElAPO).

2    Metalloaluminophosphate molecular sieves are described in U.S. Patent

3    Nos. 4,500,651; 4,567,029; 4,544,143; 4,686,093 and 4,861,743. Nonmetal

4    substituted aluminophosphates are described in U.S. Patent No. 4,973,785.

5            Methods for forming a non-zeolitic molecular sieves may be found, for

6    example, in U.S. Patent Nos. 4,440,871; 4,710,485; and 4,973,785. Non-

7    zeolitic molecular sieves are generally synthesized by hydrothermal

8    crystallization from a reaction mixture comprising reactive sources of

9    aluminum, phosphorus, optionally one or more elements, other than

10   aluminum and phosphorous, which are capable of forming oxides in

11   tetrahedral coordination with $AlO_2$ and $PO_2$ units, and one or more organic

12   templating agents. The reaction mixture is placed in a sealed pressure vessel

13   and heated, preferably under autogenous pressure at a temperature of at

14   least about 100°C., and preferably between 100°C. and 250°C., until crystals

15   of the molecular sieve product are obtained, usually for a period of from 2

16   hours to 2 weeks.

17           A silicoaluminophosphate molecular sieve is suitable as an

18   intermediate pore size molecular sieve for the present process. The

19   silicoaluminophosphate molecular sieves belong to a class of non-zeolitic

20   molecular sieves characterized by a three-dimensional microporous

21   framework structure of $AlO_2$, and $PO_2$ tetrahedral oxide units with a unit

22   empirical formula on an anhydrous basis of:

23                          $(Si_xAl_yP_z)O_2$

24   wherein "x", "y", and "z" represent the mole fractions, respectively, of silicon,

25   aluminum, and phosphorus, wherein "x" has a value equal to or greater than

26   zero (0), and "y" and "z" each have a value of at least 0.01.

27           Catalytic particulates containing at least one of the intermediate pore

28   molecular sieves SAPO-11, SAPO-31 and SAPO-41 are particularly useful in

29   the present process. U.S. Patent No. 4,440,871 describes SAPO's generally

30   and SAPO-11, SAPO-31, and SAPO-41 specifically. The most preferred

1    intermediate pore size silicoaluminophosphate molecular sieve for use in the

2    process of the invention is SAPO-11. When combined with a platinum or

3    palladium hydrogenation component, the SAPO-11 converts the waxy

4    components to produce a lubricating oil having excellent yield, very low pour

5    point, low viscosity and high viscosity index.

6    SAPO-11 comprises a silicoaluminophosphate material having a

7    three-dimensional microporous crystal framework structure of $PO_2$, $AlO_2$ and

8    $SiO_2$ tetrahedral units whose unit empirical formula on an anhydrous basis is:

$$mR: (Si_xAl_yP_z)O_2$$

9

10   wherein "R" represents at least one organic templating agent present in the

11   intracrystalline pore system; "m" represents the moles of "R" present per mole

12   of $(Si_xAl_yP_z)O_2$ and has a value of from zero to about 0.3, "x", "y" and "z"

13   represent respectively, the mole fractions of silicon, aluminum and

14   phosphorous, wherein "x" has a value greater than zero (0), and "y" and "z"

15   each have a value of at least 0.01. The silicoaluminophosphate has a

16   characteristic X-ray powder diffraction pattern which contains at least the

17   d-spacings (as-synthesized and calcined) set forth below in Table I. When

18   SAPO-11 is in the as-synthesized form, "m" preferably has a value of from

19   0.02 to 0.3.

### TABLE I

| $2\Theta$ | Interplanar d-spacings (Å) | Relative Intensity, $I/I_o$ |
|---|---|---|
| 9.4-9.65 | 9.41-9.17 | m |
| 20.3-20.6 | 4.37-4.31 | m |
| 21.0-21.3 | 4.23-4.17 | vs |
| 22.1-22.35 | 4.02-3.99 | m |
| 22.5-22.9 (doublet) | 3.95-3.92 | m-s |

28   The most particularly preferred intermediate pore SAPO prepared by

29   the present process is SM-3, which has a crystalline structure falling within

30   that of the SAPO-11 molecular sieves. The preparation of SM-3 and its

31   unique characteristics are described in U.S. Patent Nos. 4,943,424 and

1    5,158,665. The entire disclosure of each of these patents is incorporated

2    herein by reference for all purposes.

3          Another intermediate pore size silicoaluminophosphate molecular

4    sieve preferably used in the process of the invention is SAPO-31. SAPO-31

5    comprises a silicoaluminophosphate having a three-dimensional microporous

6    crystal framework of $PO_2$, $AlO_2$ and $SiO_2$ tetrahedral units whose unit

7    empirical formula on an anhydrous basis is:

8                                $mR: (Si_xAl_yP_z)O_2$

9    wherein R represents at least one organic templating agent present in the

10   intracrystalline pore system; "m" represents the moles of "R" present per mole

11   of $(Si_xAl_yP_z)O_2$ and has a value of from zero to 0.3; "x", "y" and "z" represent,

12   respectively, the mole fractions of silicon, aluminum and phosphorous,

13   wherein "x" has a value greater than zero (0), and "y" and "z" each have a

14   value of at least 0.01. The silicoaluminophosphate has a characteristic X-ray

15   powder diffraction pattern (as-synthesized and calcined) which contains at

16   least the d-spacings set forth below in Table II. When SAPO-31 is in the

17   as-synthesized form, "m" preferably has a value of from 0.02 to 0.3.

18                                    TABLE II

| $2\Theta$ | Interplanar d-spacings (Å) | Relative Intensity, $I/I_o$ |
|---|---|---|
| 8.5-8.6 | 10.40-10.28 | m-s |
| 20.2-20.3 | 4.40-4.37 | m |
| 21.9-22.1 | 4.06-4.02 | w-m |
| 22.6-22.7 | 3.93-3.92 | vs |
| 31.7-31.8 | 3.823-2.814 | w-m |

27          SAPO-41, also suitable for use in the process of the invention,

28   comprises a silicoaluminophosphate having a three-dimensional microporous

29   crystal framework structure of $PO_2$, $AlO_2$ and $SiO_2$ tetrahedral units, and

30   whose unit empirical formula on an anhydrous basis is:

31                               $mR:(Si_xAl_yP_z)O_2$

32   wherein R represents at least one organic templating agent present in the

33   intracrystalline pore system; "m" represents the moles of "R" present per mole

1 of $(Si_xAl_yP_z)O_2$ and has a value of from zero to 0.3; "x", "y" and "z" represent,

2 respectively, the mole fractions of silicon, aluminum and phosphorous,

3 wherein "x" has a value greater than zero (0), and "y" and "z" each have a

4 value of at least 0.01. SAPO-41 has characteristic X-ray powder diffraction

5 pattern (as-synthesized and calcined) which contains at least the d-spacings

6 set forth below in Table III. When SAPO-41 is in the as-synthesized form,

7 "m" preferably has a value of from 0.02 to 0.03.

TABLE III

8

| $2\Theta$ | Interplanar d-spacings (Å) | Relative Intensity, $I/I_o$ |
|---|---|---|
| 13.6-13.8 | 6.51-6.42 | w-m |
| 20.5-20.6 | 4.33-4.31 | w-m |
| 21.1-21.3 | 4.21-4.17 | vs |
| 22.1-22.3 | 4.02-3.99 | m-s |
| 22.8-23.0 | 3.90-3.86 | m |
| 23.1-23.4 | 3.82-3.80 | w-m |
| 25.5-25.9 | 3.493-3.44 | w-m |

18 The group of intermediate pore size zeolites useful in the present

19 process include ZSM-22, ZSM-23, ZSM-35, ZSM-48 and SSZ-32. These

20 catalysts are generally considered to be intermediate pore size catalysts

21 based on the measure of their internal structure as represented by their

22 Constraint Index. Zeolites which provide highly restricted access to and

23 egress from their internal structure have a high value for the Constraint Index,

24 while zeolites which provide relatively free access to the internal zeolite

25 structure have a low value for their Constraint Index. The method for

26 determining Constraint Index is described fully in U.S. Pat. No. 4,016,218

27 which is incorporated herein by reference.

28 One of the zeolites of the present invention, ZSM-22, is a highly

29 siliceous material which includes crystalline three-dimensional continuous

30 framework silicon containing structures or crystals which result when all the

31 oxygen atoms in the tetrahedra are mutually shared between tetrahedral

-16-

1    atoms of silicon or aluminum, and which can exist with a network of mostly

2    SiO$_2$, i.e., exclusive of any intracrystalline cations. The description of ZSM-22

3    is set forth in full in U.S. Pat. No. 4,556,477, U.S. Pat. No. 4,481,177 and

4    European Patent Application No. 102,716 the contents of which are

5    incorporated herein by reference.

6          As indicated in U.S. Pat. No. 4,566,477, the crystalline material

7    ZSM-22 has been designated with a characteristic X-ray diffraction pattern as

8    set forth in Table IV.

9                               TABLE IV

10                      Most Significant Lines of ZSM-22

| Interplanar d-spacings (Å) | Relative Intensity (I/Io) |
|---|---|
| 10.9 ± 0.2 | m-vs |
| 8.7 ± 0.16 | w |
| 6.94 ± 0.10 | w-m |
| 5.40 ± 0.08 | w |
| 4.58 ± 0.07 | w |
| 4.36 ± 0.07 | vs |
| 3.68 ± 0.05 | vs |
| 3.62 ± 0.05 | s-vs |
| 3.47 ± 0.04 | m-s |
| 3.30 ± 0.04 | w |
| 2.74 ± 0.02 | w |
| 2.52 ± 0.02 | w |

26          It should be understood that the X-ray diffraction pattern of Table VII is

27    characteristic of all the species of ZSM-22 zeolite compositions. Ion

28    exchange of the alkali metal cations with other ions results in a zeolite which

29    reveals substantially the same X-ray diffraction pattern with some minor shifts

30    in interplanar spacing and variation in relative intensity.

31          Furthermore, the original cations of the as-synthesized ZSM-22 can be

32    replaced at least in part by other ions using conventional ion exchange

33    techniques. It may be necessary to pre-calcine the ZSM-22 zeolite crystals

34    prior to ion exchange. In accordance with the present invention, the

1 replacement ions are those taken from Group VIII of the Periodic Table,

2 especially platinum, palladium, iridium, osmium, rhodium and ruthenium.

3     ZSM-22 freely sorbs normal hexane and has a pore dimension greater

4 than about 4Å. In addition, the structure of the zeolite provides constrained

5 access to larger molecules. The Constraint Index as determined by the

6 procedure set forth in U.S. Pat. No. 4,016,246 for ZSM-22 has been

7 determined to be from about 2.5 to about 3.0.

8     Another zeolite which can be used with the present invention is the

9 synthetic crystalline aluminosilicate referred to as ZSM-23, disclosed in U.S.

10 Pat. No. 4,076,842, the contents of which are incorporated herein by

11 reference. The ZSM-23 composition has a characteristic X-ray diffraction

12 pattern as set forth herein in Table V.

13

## TABLE V

| Interplanar d-spacings (Å) | Relative Intensity, $I/I_o$ |
|---|---|
| 11.2 ±0.23 | m |
| 10.1 ±0.20 | w |
| 7.87 ±0.15 | w |
| 5.59 ±0.10 | w |
| 5.44 ±0.10 | w |
| 4.90 ±0.10 | w |
| 4.53 ±0.10 | s |
| 3.90 ±0.08 | vs |
| 3.72 ±0.08 | vs |
| 3.62 ±0.07 | vs |
| 3.54 ±0.07 | m |
| 3.44 ±0.07 | s |
| 3.36 ±0.07 | w |
| 3.16 ±0.07 | w |
| 3.05 ±0.06 | w |
| 2.99 ±0.06 | w |
| 2.85 ±0.06 | w |
| 2.54 ±0.05 | m |
| 2.47 ±0.05 | w |
| 2.40 ±0.05 | w |
| 2.34 ±0.05 | w |

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1   The ZSM-23 composition can also be defined in terms of mole ratios of

2   oxides in the anhydrous state as follows:

3          $(0.58\text{-}3.4)M_{2/n}O: Al_2O_3:(40\text{-}250)SiO_2$
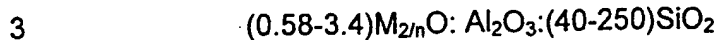
4   wherein M is at least 1 cation and n is the valence thereof. As in the ZSM-22,

5   the original cations of as-synthesized ZSM-23 can be replaced in accordance

6   with techniques well-known in the art, at least in part by ionic exchange with

7   other cations. In the present invention these cations include the Group VIII

8   metals as set forth hereinbefore.

9      Another intermediate pore size zeolite which has been found to be

10   successful in the present invention is ZSM-35, which is disclosed in U.S.

11   Patent No. 4,016,245, the contents of which are incorporated herein by

12   reference. The synthetic crystalline aluminosilicate known as ZSM-35, has a

13   characteristic X-ray diffraction pattern which is set forth in U.S. Pat.

14   No. 4,016,245. ZSM-35 has a composition which can be defined in terms of

15   mole ratio of oxides in the anhydrous state as follows:

16          $(0.3\text{-}2.5)R_2O:(0\text{-}0.8)M_2O:Al_2O_3:>8SiO_2$
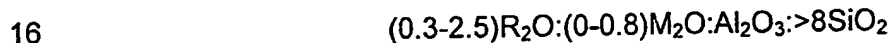
17   wherein R is organic nitrogen-containing cation derived from ethylenediamine

18   or pyrrolidine and M is an alkali metal cation. The original cations of the

19   as-synthesized ZSM-35 can be removed using techniques well known in the

20   art which includes ion exchange with other cations. In the present invention,

21   the cation exchange is used to replace the as-synthesized cations with the

22   Group VIII metals set forth herein. It has been observed that the X-ray

23   diffraction pattern of ZSM-35 is similar to that of natural ferrierite with a

24   notable exception being that natural ferrierite patterns exhibit a significant line

25   at 1.33Å.

26      Another intermediate pore size zeolite which has been found to be

27   successful in the present invention is SSZ-32, which is disclosed in U.S.

28   Patent No. 5,053,373, the content of which are incorporated herein by

29   reference. SSZ-32 has a characteristic X-ray diffraction pattern which is set

30   forth in U.S. Patent No. 5,053,373. The composition of SSZ-32, as

1  synthesized and in the anhydrous state, in terms of mole ratios of oxides, is

2  as follows:

3  $(0.05\text{-}2.0)R_2O:(0.1\text{-}2.0)M_2O:Al_2O_3:(20\text{-less than }40)SiO_2$

4  where M is an alkali metal cation and R is an organic nitrogen-containing

5  cation, such as an N-lower alkyl-N-N'-isopropyl-imidazolium cation. SSZ-32

6  has a mole ratio of silicon oxide to aluminum oxide in the range of 20 to less

7  than 40, and has essentially the same X-ray diffraction pattern of ZSM-23.

8  Hydroconversion processes using SSZ-32 are disclosed, for example, in U.S.

9  Patent Nos. 5,300,210 and in 5,397,454.

10  ZSM-48 is a crystalline aluminosilicate zeolite which is suitable as a

11  dewaxing catalyst for the present invention. Zeolite ZSM-48 is disclosed in

12  U.S. Patent No. 4,585,747, the entire disclosure of which is incorporated

13  herein by reference for all purposes, and has a characteristic X-ray diffraction

14  pattern as set forth in Table VI.

15

16  Table VI

| Interplanar d-spacings (Å) | Relative Intensity, I/I₀ |
|---|---|
| $11.8 \pm 0.2$ | s |
| $10.2 \pm 0.2$ | w-m |
| $7.2 \pm 0.15$ | w |
| $4.2 \pm 0.08$ | vs |
| $3.9 \pm 0.08$ | vs |
| $3.6 \pm 0.06$ | w |
| $3.1 \pm 0.05$ | w |
| $2.85 \pm 0.05$ | w |

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28  Zeolite ZSM-48 can also be identified, in terms of mole ratios of oxides and in

29  the anhydrous state, as follows:

30  $(0.1 \text{ to } 4)R_2O:(0.01 \text{ to } 2)M_{2/n}O:(0 \text{ to } 0.5)Al_2O_3:(100)SiO_2$

1    wherein M is at least one cation having a valence n and R is the cation. The

2    cation taught in U.S. Patent No. 4,585,747 is derived from the monomeric,

3    diquaternary compound bis(N-methylpyridyl)ethylinium.

4         Other molecular sieves which can be used with the present invention

5    include, for example, Theta-1, as described in U.S. Pat. Nos. 4,533,649 and

6    4,836,910, both of which are incorporated in their entireties by reference,

7    Nu-10, as described in European Patent Application 065,400 which is

8    incorporated in its entirety by reference and SSZ-20 as described in U.S. Pat.

9    No. 4,483,835 which is incorporated in its entirety by reference.

10   X-ray crystallography of SAPO-11, SAPO-31, SAPO-41, ZSM-22, ZSM-23

11   and ZSM-35 shows these molecular sieves to have the following major and

12   minor axes: SAPO-11, major 6.3Å, minor 3.9Å; (Bennett, J. M., et al, Zeolites,

13   1, 160(87)), SAPO-31 and SAPO-41, believed to be slightly larger than

14   SAPO-11, ZSM-22, major 5.5Å, minor 4.5Å (Kokotailo, G. T., et al, Zeolites,

15   5, 349(85)); ZSM-23, major 5.6Å, minor 4.5Å; ZSM-35, major 5.4Å, minor

16   4.2Å. ZSM-48 is a molecular sieve having a 10-ring structure with 1-D pores

17   having a 5.23 Å major axis and a 5.11 Å minor axis. (Meier, W. M. and

18   Olsen, D. H., Atlas of Zeolite Structure Types, Butterworths, 1987).

19        It is preferred that relatively small crystal size catalyst be utilized in

20   practicing the invention. Suitably, the average crystal size is no greater than

21   about 10 microns (i.e. micrometers), preferably no more than about 5

22   microns, more preferably no more than about 1 micron and still more

23   preferably no more than about 0.5 micron.

24        The physical form of the catalyst depends on the type of catalytic

25   reactor being employed and may be in the form of a granule or powder, and is

26   desirably compacted into a more readily usable form (e.g., larger

27   agglomerates), usually with a silica or alumina binder for fluidized bed

28   reaction, or pills, prills, spheres, extrudates, or other shapes of controlled size

29   to accord adequate catalyst-reactant contact. The preferred catalyst is in the

30   form of extrudates with a cross-sectional diameter between about $1/4$ inch and

31   about $1/32$ inch. In the catalyst, the molecular sieve can be composited with

1  other material resistant to the temperatures and other conditions employed in
2  organic conversion processes. Such matrix materials include active and
3  inactive materials and synthetic or naturally occurring zeolites as well as
4  inorganic materials such as clays, silica and metal oxides. Additional porous
5  matrix materials include silica, alumina, titania, magnesia and mixtures
6  thereof. The matrix can be in the form of a cogel. Alumina and silica-alumina
7  matrix materials are preferred.

8      The intermediate pore size molecular sieve is used in admixture with at
9  least one Group VIII metal. Preferably, the Group VIII metal is selected from
10  the group consisting of at least one of platinum and palladium and optionally,
11  other catalytically active metals such as molybdenum, nickel, vanadium,
12  cobalt, tungsten, zinc and mixtures thereof. Most preferably, the Group VIII
13  metal is selected from the group consisting of at least one of platinum and
14  palladium. The amount of metal ranges from about 0.01% to about 10% by
15  weight of the molecular sieve, preferably from about 0.1% to about 5% by
16  weight and more preferably from about 0.2% to about 1% by weight of the
17  molecular sieve. The techniques of introducing catalytically active metals into
18  a molecular sieve are disclosed in the literature, and preexisting metal
19  incorporation techniques and treatment of the molecular sieve to form an
20  active catalyst such as ion exchange, impregnation or occlusion during sieve
21  preparation are suitable for use in the present process. Such techniques are
22  disclosed in U.S. Pat. Nos. 3,236,761; 3,226,339; 3,236,762; 3,620,960;
23  3,373,109; 4,202,996; 4,440,781 and 4,710,485; and in U.S. Application
24  Serial No. 08/728818; the entire disclosures of which are incorporated herein
25  by reference for all purposes.

26      The term "metal" or "active metal" as used herein means one or more
27  metals in the elemental state or in some form such as sulfide, oxide and
28  mixtures thereof. Regardless of the state in which the metallic component
29  actually exists, the concentrations are computed as if they existed in the
30  elemental state.

1       The catalyst may also contain metals which reduce the number of

2   strong acid sites on the catalyst and thereby lower the selectivity for cracking

3   versus isomerization. Especially preferred are the Group IIA metals such as

4   magnesium and calcium. The Group VIII metal utilized in the process of this

5   invention can mean one or more of the metals in its elemental state or in

6   some form such as the sulfide or oxide and mixtures thereof. As is customary

7   in the art of catalysis, when referring to the active metal or metals, it is

8   intended to encompass the existence of such metal in the elementary state or

9   in some form such as the oxide or sulfide as mentioned above, and

10   regardless of the state in which the metallic component actually exists, the

11   concentrations are computed as if they existed in the elemental state.

12       The catalytic isomerization step of the invention may be conducted by

13   contacting the feed with a fixed stationary bed of catalyst, with a fixed

14   fluidized bed, or with a transport bed. A simple and therefore preferred

15   configuration is a trickle-bed operation in which the feed is allowed to trickle

16   through a stationary fixed bed, preferably in the presence of hydrogen.

17       The catalytic isomerization conditions employed depend on the feed

18   used and the desired pour point. Generally, the temperature is from about

19   200°C to about 475°C, preferably from about 250°C and to about 450°C. The

20   pressure is typically from about 15 psig ( 103 kPa) to about 2500 psig (27.2

21   MPa), preferably from about 50 psig (345 kPa) to about 2000 psig (13.8

22   MPa), more preferably from about 100 psig to about 1500 psig (10.3 MPa).

23   The liquid hourly space velocity (LHSV) is preferably from about $0.1hr^{-1}$ to

24   about 20 $hr^{-1}$, more preferably from about $0.1hr^{-1}$ to about $5hr^{-1}$, and most

25   preferably from about $0.1hr^{-1}$ to about 1.0 $hr^{-1}$. Low pressure and low liquid

26   hourly space velocity provide enhanced isomerization selectivity which results

27   in more isomerization and less cracking of the feed thus producing an

28   increased yield.

29       Hydrogen is preferably present in the reaction zone during the catalytic

30   isomerization process. The hydrogen to feed ratio is typically from about 500 .

31   to about 30,000 SCF/bbl (standard cubic feet per barrel) (76-4540 std liters

1 H$_2$/kg oil), preferably from about 1,000 to about 10,000 SCF/bbl (151-1510 std

2 liters H$_2$/kg oil). Generally, hydrogen will be separated from the product and

3 recycled to the reaction zone. Strong acidity may also be reduced by

4 introducing nitrogen compounds, e.g., NH$_3$ or organic nitrogen compounds,

5 into the feed; however, the total nitrogen content should be less than 50 ppm,

6 preferably less than 10 ppm.

7 In the dewaxing process using the catalyst of the present invention, the

8 pour point of the isomerized product is lower than the pour point of the waxy

9 feed to the dewaxing process. For oils of commercial interest, the pour point

10 of the oil is generally below about 10°C, and often below 0°C. While a low

11 pour point is desired in the product from the isomerization step, excessive

12 isomerization has a detrimental effect on product viscosity index, as

13 described hereinbefore. The wax content of the isomerized oil is between

14 about 1% and about 40%, preferably between about 3% and about 20%, of

15 the wax content of the waxy feed. The isomerization step, then preferentially

16 removes between about 60% and about 99% by weight of the wax contained

17 in the waxy feedstock. Thus, the pour point of the isomerized product, while

18 being substantially lower than the pour point of the feed to the isomerization

19 process, will be at least about 6°C, and more usually at least about 12°C

20 above the target pour point set for the finished lubricating oil base stock. The

21 viscosity index of the isomerized product will be generally above about 140

22 and preferably above about 150. With some products, a viscosity index of

23 160 or above is possible.

24 The wax content of the oil set forth herein is determined from a

25 conventional solvent dewaxing method. An example method is as follows:

26 300 g of oil is diluted 50/50 with a 4:1 mixture of methyl ethyl ketone

27 and toluene which is cooled to –20°C in a refrigerator. The mixture is filtered

28 through a Coors funnel at –15 °C. using Whatman No. 3 filter paper. The wax

29 is removed from the filter and placed in a tared 2 liter flask. The solvent is

30 removed on a hot plate and the wax weighed.

1    The present integrated two-step process comprises a catalytic

2    isomerization step and a solvent dewaxing step. Following the isomerization

3    of the waxy feed, the pour point of the isomerized oil will generally be at least

4    about 6°C and preferably at least about 12°C above a target pour point of the

5    finished oil. Continued isomerization results in unselective isomerization and

6    the formation of increased numbers of triply branched paraffins, resulting in a

7    reduced viscosity index. Thus, the isomerized oil is solvent dewaxed to a

8    desired target pour point, which is determined by the particular grade of oil

9    which is being produced. The target pour point will generally be less than or

10   equal to about -10°C. For high quality oils, a pour point less than or equal to

11   about -20°C or even less than or equal to about -30°C may be preferred.

12   Depending on the dewaxing conditions and the feeds used for the dewaxing

13   process, a viscosity index above 140 can be achieved. Lubricating oil stocks

14   will generally boil above 230°C (450°F), more usually above 315°C (600°F).

15   Conventional solvent dewaxing processes which are commonly used in

16   the preparation of a lubricating oil base stock are suitable for the present

17   integrated process. Such processes include crystallization of the wax from a

18   chilled mixture of waxy oil and a solvent such as a blended methyl ethyl

19   ketone/toluene solvent. The slack wax and/or the foots oil recovered as the

20   residual oil remaining in the slack wax may be recovered or recycled to the

21   isomerization reaction zone. The isomerized oil which is the feed to the

22   solvent dewaxing step of the present process will generally have a pour point

23   of less than about 40°C, and a viscosity index of greater than about 125 and

24   preferably greater than about 140, and more preferably greater than about

25   150.

26   Feed to the isomerization process may require pretreatment before it

27   can be satisfactorily processed in the isomerization step. The pretreatment

28   steps remove heteroatoms such as nitrogen and sulfur which might poison

29   the isomerization catalyst, or low viscosity index components such as

30   aromatics and polycyclic naphthenes. A typical hydrocracking process is

1   described, for example, in U.S. Patent No. 5,158,665, the entire disclosure of

2   which is already incorporated by reference.

3        It may further be desired to hydrofinish the dewaxed oil in a mild

4   hydrogenation process to produce more stable lubrication oils. The

5   hydrofinishing can be conventionally carried out in the presence of a metallic

6   hydrogenation catalyst, for example, platinum on alumina. The hydrofinishing

7   can be carried out at a temperature of from about 190°C to about 340°C and

8   a pressure of from about 400 psig to about 3000 psig (2.76-20.7 MPa). A

9   description of a typical hydrofinishing process and catalyst which is useful in

10   the present process is taught in U.S. Patent No. 5,158,665. Hydrofinishing in

11   this manner is also described in U.S. Pat. 3,852,207, both of which are

12   incorporated herein by reference for all purposes.

13        The present process is suitable for preparing very high viscosity index

14   lubricating oil base stocks having a wide range of viscosities, including base

15   stocks having a viscosity, measured at 100°C, of 10 cSt or higher. These

16   base oils have a viscosity index of at least about 140 (preferably at least

17   about 150 and more preferably at least about 160), and a pour point of less

18   than or equal to about -10°C (preferably less than or equal to about -20°C,

19   and more preferably less than or equal to about -30°C). A particularly

20   important base oil prepared in the present process has a viscosity, measured

21   at 100°C, of about 3 cSt or less, preferably less than about 3 cSt, and a

22   viscosity index of at least about 140, preferably at least about 150, and more

23   preferably at least about 160. This relatively light oil prepared in the present

24   process has a viscosity index higher than that produced even in synthetic oils

25   having a viscosity, measured at 100°C, of about 3 cSt or less.

26                   EXAMPLES

27              Comparative Example A

28        Tetracosane (n-$C_{24}$, purchased from Aldrich), which had a pour point of

29   +50 C and a viscosity at 100 C of about 2.5 cSt, was isomerized over SM-3

30   impregnated with 0.5 wt% Pt. The catalyst was pelleted, then crushed to 24-

1    42 mesh for testing.  The catalyst was sulfided in situ prior to testing by

2    injecting $H_2S$ through a septum into the hydrogen line ahead of the reactor.

3    Isomerization was carried out in a continuous feed high pressure pilot plant

4    with once-through hydrogen gas.  Run conditions were 1000 psig total

5    pressure (6.89 MPa), 0.6 $hr^{-1}$ LHSV, and 6.7 MSCF/bbl $H_2$  (1010 std liters

6    $H_2$/kg oil) At a pour point of -25°C, the viscosity index of the 316°C+

7    distillation bottoms was 132 (Table VII).

8                            <u>Example 1</u>

9       Tetracosane was isomerized over the same Pt/SM-3 catalyst as in

10   Comparative Example A, but to a pour point of +20 °C.  The 316 °C+

11   distillation bottoms were then solvent dewaxed (SDW) to a pour point of –29

12   °C. The viscosity index of the oil was 148 (Table VII), much higher (about 18

13   numbers) than obtained with isomerization only to the same pour point

14   (Figure I).  In addition, the isomerized and solvent dewaxed oil had a much

15   lower average number of branches per molecule.

1

TABLE VII
ISOMERIZATION OF n-C$_{24}$ OVER Pt/SM-3 AT
1000 PSIG (6.99 MPa), 0.6 hr$^{-1}$ LHSV,
AND 6.7 MSCF/BBL H$_2$ (1010 std liters H$_2$/kg oil)

| | Comparative Example A | | Example 1 |
|---|---|---|---|
| Temperature, °C | 321 | 332 | 324 |
| n-C$_{24}$ Conversion, wt% | 99.1 | 99.6 | 95.1 |
| Yield, Wt% | | | |
| C4- | 0.5 | 0.9 | 0.2 |
| C5-82 °C | 1.9 | 2.3 | 0.5 |
| 82-177 °C | 2.8 | 3.2 | 1.7 |
| 177-316°C | 8.2 | 12.3 | 4.3 |
| 316 °C+ | 86.6 | 81.3 | 93.3 |
| 316°C+ Distillation Yield, wt% | 87.4 | 82.2 | 92.1 |
| Solvent Dewax | No | No | Yes |
| Oil, wt% | | | 65.6 |
| Wax, wt% | | | 32.4 |
| Pour Point Before SDW, °C | | | +20 |
| 316°C+ Lube Yield, wt% | 86.6 | 81.3 | 61.2 |
| 316 °C+ Lube Inspections | | | |
| Pour Point, °C | -15 | -25 | -29 |
| Cloud Point, °C | -1 | -8 | -9 |
| Viscosity, 40 °C, cSt | 8.636 | 8.372 | 8.313 |
| 100 °C, cSt | 2.579 | 2.507 | 2.556 |
| VI | 137 | 132 | 148 |
| Avg. Branches/Molecule | 1.83 | 1.97 | 1.63 |
| Simulated Distillation, LV%, °C | | | |
| St/5 | 277/358 | 294/357 | 304/369 |
| 30/50 | 368/379 | 368/379 | 374/382 |
| 50 | 384 | 384 | 385 |
| 70/90 | 388/392 | 388/391 | 388/391 |
| 95/EP | 392/394 | 393/394 | 392/398 |

Comparative Example B

An extrudate catalyst containing 85 wt% SM-3 sieve and 15 wt% Catapal alumina binder was impregnated with 0.4 wt% Pt and crushed to 24-42 mesh (0.35-0.70 mm). It was used to isomerize a 7.8 cSt heavy neutral slack wax (Table VIII) at 0.5 LHSV hr$^{-1}$, 1000 psig (6.99 MPa), and 8 MSCF/bbl H$_2$ (1210 std liters H$_2$/kg oil). Results are given in Table IX, showing a 144 VI at a pour point of -12°C.

## Example 2

Comparative Example B was repeated, except in this case, the feed was isomerized over the SM-3 catalyst to a pour point of 0°C, followed by solvent dewaxing to –18°C. The viscosity index (143, Table IX) was about the same as in the comparative example, but the pour point was lower. In addition, the cloud point was considerably lower.

TABLE VIII
INSPECTIONS OF HEAVY NEUTRAL SLACK WAX

| | |
|---|---|
| Sulfur, ppm | 7.0 |
| Viscosity, 100 °C, cSt | 7.818 |
| Simulated Distillation, LV%, °C | |
| St/5 | 198/371 |
| 30/50 | 392/439 |
| 50 | 476 |
| 70/90 | 522/594 |
| 95/EP | 628/696 |

TABLE IX
ISOMERIZATION OF HEAVY NEUTRAL SLACK WAX
AT 0.5 hr$^{-1}$ LHSV, 1000 PSIG (6.99 MPa),
AND 8 MSCF/BBL H$_2$ (1210 std liters H$_2$/kg oil)
OVER Pt/SM-3 CATALYST

|  | Comparative Example B | Example 2 |
|---|---|---|
| Temperature, °C | 349 | 332 |
| 343°F+ Conversion, wt% | 27.4 | 21.9 |
| Wax Conversion, wt% | 100 | 84.1 |
| Selectivity to Lube, wt% | 67.4 | 72.6 |
| Pour Point before SDW, °C |  | 0 |
| Solvent Dewax | No | Yes |
| Oil, wt% |  | 86.2 |
| Wax, wt% |  | 13.8 |
| 650 F+ Lube Yield, wt% | 67.4 | 61.1 |
| Pour Point, °C | -12 | -18 |
| Cloud Point, °C | +9 | -17 |
| Viscosity, 40 °C, cSt | 41.42 | 37.50 |
| 100 °C, cSt | 7.367 | 6.836 |
| VI | 144 | 143 |
| Simulated Distillation, LV%, °C |  |  |
| St/5 | 193/357 | 226/358 |
| 30/50 | 378/425 | 377/419 |
| 50 | 464 | 456 |
| 70/90 | 511/585 | 500/579 |
| 95/EP | 617/717 | 629/747 |

Comparative Example C

An SM-3 catalyst similar to that of Comparative Example B was used
to isomerize a hydrotreated 4.5 cSt slack wax (Table X) at 0.5 hr$^{-1}$ LHSV, 800
psig total pressure (5.61 MPa), and 3 MSCF/bbl H$_2$ (454 std liters H$_2$/kg oil).
Results are given in Table XI, showing a 140 VI at a pour point of −7°C.

-30-

Example 3

Comparative Example C was repeated, except in this case, the feed was isomerized at 1100 psig (7.58 MPa) over the SM-3 catalyst to a pour point of –3°C, followed by solvent dewaxing to –14°C. The viscosity index (144, Table XI) was higher than in the comparative example, and the pour point was lower.

TABLE X
INSPECTIONS OF HYDROTREATED SLACK WAX

| | | |
|---|---|---|
| Density | | 0.84 g/cm$^3$ |
| Sulfur, ppm | | 33 |
| Nitrogen, ppm | | 0.3 |
| | | |
| Pour Point, °C | | +39 |
| | | |
| Viscosity, | 70 °C, cSt | 8.120 |
| | 100 °C, cSt | 4.465 |
| Wax, wt% | | 58.2 |
| | | |
| Dewaxed Oil Properties | | |
| Pour Point, °C | | -8 |
| Cloud Point, °C | | -8 |
| | | |
| Viscosity, | 40 °C, cSt | 21.82 |
| | 100 °C, cSt | 4.609 |
| VI | | 130 |

## TABLE XI
### ISOMERIZATION OF HYDROTREATED SLACK WAX
### AT 0.5 hr$^{-1}$ LHSV AND 3 MSCF/BBL H$_2$ (450 std liters H$_2$/kg oil)
### OVER Pt/SM-3 CATALYST

| | Comparative Example C | Example 3 |
|---|---|---|
| Temperature, °C | 327 | 327 |
| Pressure, MPa | 5.61 | 7.68 |
| | | |
| Conversion <371°C, wt% | 28.9 | 23.7 |
| | | |
| Yields, Wt% | | |
| C4- | 2.2 | 2.0 |
| C5-82 °C | 3.8 | 3.3 |
| 180-371 °C | 31.7 | 27.8 |
| 371°C+ | 62.8 | 67.3 |
| | | |
| 371°C+ Yield, Wt% | 62.6 | 66.8 |
| | | |
| Pour Point before SDW, °C | | -3 |
| | | |
| Solvent Dewax | No | Yes |
| Oil, wt% | | 96 |
| Wax, wt% | | 4 |
| | | |
| 371°C+ Lube Yield, wt% | 62.6 | 64 |
| | | |
| Pour Point, °C | -7 | -14 |
| Cloud Point, °C | -4 | -11 |
| | | |
| Viscosity, 40 °C, cSt | 22.0 | 21.98 |
| 100 °C, cSt | 4.746 | 4.785 |
| VI | 140 | 144 |
| | | |
| Simulated Distillation, LV%, °C | | |
| ST/5 | 287/368 | 294/371 |
| 30/50 | 436/452 | 738/454 |
| 95/99 | 486/501 | 488/502 |

1                           <u>Comparative Example D</u>

2          An extrudate catalyst containing 65 wt% SSZ-32 zeolite and 35 wt%

3 Catapal alumina binder was impregnated with 0.35 wt% Pt and crushed to 24-

4 42 mesh (0.35-0.70 mm). After pre-sulfiding with $H_2S$, it was used to

5 isomerize tetracosane at 0.6 $hr^{-1}$ LHSV, 1000 psig (6.99 MPa), and 6.7

6 MSCF/bbl $H_2$ (1010 std liters $H_2$/kg oil). Results are given in Table XII,

7 showing a 152 VI at a pour point of –9°C and a 143 VI at a pour point of –

8 33°C.

9                                 Example 4

10          Comparative Example D was repeated, except in this case, the feed

11 was isomerized over the SSZ-32 catalyst to a pour point of +4°C, followed by

12 solvent dewaxing to –21°C. The viscosity index (156, Table XII) was higher

13 than in the comparative example by an estimated 8-9 numbers at the same

14 pour point.

TABLE XII

ISOMERIZATION OF n-C$_{24}$
AT 1000 PSIG (6.99 MPa), 0.6 hr$^{-1}$ LHSV,
AND 6.7 MSCF/BBL H$_2$ (1010 std liters h2/kg oil)
OVER Pt/SSZ-32 CATALYST

|  | Comparative Example D | | Example 4 |
|---|---|---|---|
| Temperature, °C | 307 | 324 | 310 |
| n-C$_{24}$ Conversion, wt% | 98.9 | 99.8 | 87.9 |
| | | | |
| Yields, Wt% | | | |
| C1-C2 | 0.3 | 0.4 | 0.3 |
| C3-C4 | 4.7 | 5.4 | 1.8 |
| C5-82 °C | 7.4 | 8.4 | 2.7 |
| 82-177 °C | 11.9 | 12.0 | 2.8 |
| 177-316 °C | 12.2 | 14.8 | 8.8 |
| 316 °C+ | 63.5 | 59.0 | 82.7 |
| | | | |
| 316 °C+ Distillation Yield, Wt% | 64.4 | 68.5 | 88.9 |
| | | | |
| Solvent Dewax | No | No | Yes |
| Oil, Wt% | | | 86.1 |
| Wax, Wt% | | | 11.5 |
| | | | |
| Pour Point before SDW, °C | | | +4 |
| | | | |
| 316 °C+ Lube Yield, Wt% | 63.5 | 59.0 | 52.9 |
| | | | |
| 316 °C+ Lube Inspections | | | |
| Pour Point, °C | -9 | -33 | -21 |
| Cloud Point, C | +2 | -13 | -7 |
| | | | |
| Viscosity, 40 °C, cSt | 8.028 | 6.414 | 7.669 |
| 100 °C, cSt | 2.506 | 2.121 | 2.445 |
| VI | 152 | 143 | 156 |
| | | | |
| Avg. Branches/Molecule | 1.60 | | |
| | | | |
| Simulated Distillation, LV%,°C | | | |
| St/5 | 273/333 | 156/240 | 218/294 |
| 30/50 | 371/383 | 278/373 | 373/385 |
| 50 | 387 | 380 | 389 |
| 70/90 | 390/393 | 383/387 | 391/394 |
| 95/EP | 393/395 | 388/391 | 394/394 |

1

2                                 <u>Comparative Example E</u>

3            A boron-Beta zeolite was prepared according to Example 18 of US

4     Patent No. 5,558,851. This zeolite, which had a $SiO_2/B_2O_3$ mole ratio of

5     about 60, was NH4-exchanged and then impregnated with 0.5 wt% Pt. The

6     catalyst was pelleted and crushed to 24-42 mesh (0.35-0.70 mm). After pre-

7     sulfiding with $H_2S$, the catalyst was used to isomerize tetracosane at 1000

8     psig (6.99 MPa), 0.6 $hr^{-1}$ LHSV, and 6.7 MSCF/bbl $H_2$ (1010 std liters $H_2$/kg

9     oil) to a pour point of +16°C, then solvent dewaxed to a pour point of –18°C.

10    The viscosity index after solvent dewaxing was considerably lower than for

11    the catalysts of this invention (Table XIII).

12                                 <u>Comparative Example F</u>

13           0.5 wt% Pt was impregnated on an amorphous cogelled SiO2-alumina

14    base extrudate (31 wt% SiO2, 69 wt% Al2O3). The catalyst was crushed to

15    24-42 mesh (0.35-0.70 mm) for testing. After pre-sulfiding with $H_2S$, it was

16    used to isomerize tetracosane at 1000 psig (6.99 MPa), 0.6 LHSV, and 6.7

17    MSCF/bbl $H_2$ (1010 std liters $H_2$/kg oil) to a pour point of +22°C, then solvent

18    dewaxed to a pour point of –15°C. The viscosity index after solvent dewaxing

19    was considerably lower than for the catalysts of this invention (Table XIII and

20    Figure 2). In addition, the isomerized and solvent dewaxed oil had a much

21    higher average number of branches per molecule.

TABLE XIII
ISOMERIZATION OF n-C$_{24}$
AT 1000 PSIG (6.99 MPa), 0.6 hr$^{-1}$ LHSV,
AND 6.7 MSCF/BBL H$_2$ (1010 std liters H$_2$/kg oil)

| Catalyst | Comparative Example E Pt/B-Beta | Comparative Example F Pt/SiO2-Al2O3 | Example 1 Pt/SM-3 |
|---|---|---|---|
| Temperature, °C | 319 | 329 | 324 |
| n-C$_{24}$ Conversion, Wt% | 95.2 | 92.4 | 95.1 |
| Yields, Wt% | | | |
| C4- | 2.8 | 0.3 | 0.2 |
| C5-82 °C | 5.4 | 1.3 | 0.5 |
| 82-177 °C | 7.3 | 2.0 | 1.7 |
| 177-316 °C | 16.6 | 6.7 | 4.3 |
| 316 °C+ | 67.9 | 89.7 | 93.3 |
| 316 °C+ Dist. Yield, Wt% | 69.0 | 90.3 | 92.1 |
| Solvent Dewax | Yes | Yes | Yes |
| Oil, wt% | 86.4 | 86.1 | 65.6 |
| Wax, wt% | 13.1 | 11.5 | 32.4 |
| Pour Point before SDW, °C | +16 | +22 | +20 |
| 316 °C+ Lube Yield, Wt% | 58.7 | 77.2 | 61.2 |
| 316 °C+ Lube Inspections | | | |
| Pour Point, °C | -18 | -15 | -29 |
| Cloud Point, °C | -13 | -11 | -9 |
| Viscosity, 40 °C, cSt | 8.354 | 8.364 | 8.313 |
| 100 °C, cSt | 2.517 | 2.481 | 2.556 |
| VI | 136 | 126 | 148 |
| Avg. Branches/Molecule | 1.86 | 2.02 | 1.63 |
| Simulated Dist., LV%,°C | | | |
| St/5 | 298/343 | 316/360 | 304/369 |
| 30/50 | 364/375 | 365/375 | 374/382 |
| 50 | 381 | 375 | 385 |
| 70/90 | 385/389 | 385/390 | 388/391 |
| 95/EP | 390/392 | 391/392 | 392/398 |

1  WHAT IS CLAIMED IS:

2  1. A process for preparing an oil suitable for use as a lubricating oil base
3      stock and having a viscosity index of greater than 140 and a target pour
4      point of less than or equal to −10°C comprising:

5      a) contacting a waxy feed over a catalyst comprising a molecular sieve
6        having 1-D pores with a pore diameter of between about 5.0 Å and
7        about 7.0 Å, and at least one Group VIII metal, at a pressure of from
8        about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an
9        isomerized oil having a pour point of at least 6°C above a target pour
10       point; and

11     b) solvent dewaxing the isomerized oil to produce a lubricating oil base
12       stock having the target pour point and a viscosity index of greater than
13       about 140.

14 2. The process according to Claim 1 for preparing a lubricating oil base
15     stock having a target pour point of less than about −20°C.

16 3. The process according to Claim 1 for preparing a lubricating oil base
17     stock having a viscosity index of greater than 150.

18 4. The process according to Claim 1 wherein the waxy feed contains more
19     than about 50% wax.

20 5. The process according to claim 4 wherein the waxy feed contains more
21     than about 80% wax.

22 6. The process according to Claim 1 wherein the waxy feed contains more
23     than about 70% paraffinic carbon.

24 7. The process according to Claim 1 wherein the waxy feed is selected from
25     the group consisting of synthetic oils and waxes such as those by
26     Fischer-Tropsch synthesis, high pour point polyalphaolefins, foots oils,
27     normal alpha olefin waxes, slack waxes, deoiled waxes and
28     microcrystalline waxes.

1    8.  The process according to Claim 4 wherein the waxy feed is selected from
2        the group consisting of synthetic oils and waxes such as those by
3        Fischer-Tropsch synthesis, high pour point polyalphaolefins, foots oils,
4        normal alpha olefin waxes, slack waxes, deoiled waxes and
5        microcrystalline waxes.

6    9.  The process according to Claim 1 wherein the isomerized oil has a pour
7        point of greater than about 0°C.

8    10. The process according to Claim 1 wherein between about 60% and about
9        99% by weight of the wax contained in the waxy feedstock is removed in
10       step a).

11   11. The process according to Claim 1 wherein the medium pore molecular
12       sieve has 1-D pores having a minor axis between about 3.9Å and about
13       4.8Å and a major axes between about 5.4Å and about 7.0Å.

14   12. The process according to Claim 1 wherein the medium pore molecular
15       sieve is selected from the group consisting of SAPO-11, SAPO-31 and
16       SAPO-41.

17   13. The process according to Claim 12 wherein the medium pore molecular
18       sieve is SM-3.

19   14. The process according to Claim 1 wherein the medium pore molecular
20       sieve is selected from the group consisting of ZSM-22, ZSM-23, ZSM-35
21       and SSZ-32.

22   15. The process according to Claim 14 wherein the medium pore molecular
23       sieve is SSZ-32.

24   16. The process according to Claim 1 wherein the medium pore molecular
25       sieve is ZSM-48.

26   17. The process according to Claim 1 wherein the hydrogenation component
27       is a Group VIII metal selected from the group consisting of platinum,
28       palladium or mixtures thereof.

1  18. The process according to claim 17 wherein the catalyst contains from
2      about 0.2% to about 1% by weight of the hydrogenation component.

3  19. The process of claim 1 wherein the catalyst comprising the molecular
4      sieve has sufficient isomerization selectivity such that, when contacting a
5      n-$C_{24}$ feed at a total pressure of 1000 psig (6.99 MPa), hydrogen flow
6      equivalent to 6.7 MSCF/bbl (1010 std liters $H_2$/kg oil), and a feed rate
7      equivalent to 0.6 $hr^{-1}$ LHSV with the catalyst, to produce a 316°C+
8      dewaxed product having a pour point of about +20°C and solvent
9      dewaxing the dewaxed product to a pour point of –15°C or below, an
10     isomerized product having a branching index of less than about 1.75 is
11     formed.

12 20. A process for preparing an oil suitable for use as a lubricating oil base
13     stock comprising:

14     a) contacting a waxy feed over a catalyst comprising a molecular sieve
15        having 1-D pores with a pore diameter of between about 5.0 Å and
16        about 7.0 Å, and at least one Group VIII metal, at a pressure of from
17        about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an
18        isomerized oil having a pour point of greater than about 0°C; and

19     b) solvent dewaxing the isomerized oil to produce a lubricating oil base
20        stock having a pour point of less than or equal to –10°C, a viscosity
21        index of greater than about 140 and a viscosity, measured at 100°C, of
22        about 3 cSt or less.

23 21. The process according to Claim 20 wherein the viscosity of the lubricating
24     oil base stock, measured at 100°C, is less than about 3 cSt and the pour
25     point is less than or equal to -20°C.

26 22. The process according to Claim 20 wherein the viscosity index of the
27     lubricating oil base stock is greater than 150 and the pour point is less
28     than –20°C.

29 23. The process according to Claim 20 wherein the molecular sieve is
30     SSZ-32.

1    24. The process according to Claim 20 wherein the molecular sieve is SM-3.

2    25. A lubricating oil base stock having a viscosity index of at least about 140,

3        a pour point of less than or equal to –10°C, and a viscosity, measured at

4        100°C, of about 3 cSt or less.

5    26. The lubricating oil base stock of Claim 25 having a viscosity index of at

6        least about 150 and a pour point of less than or equal to –20°C.

7

Figure 1
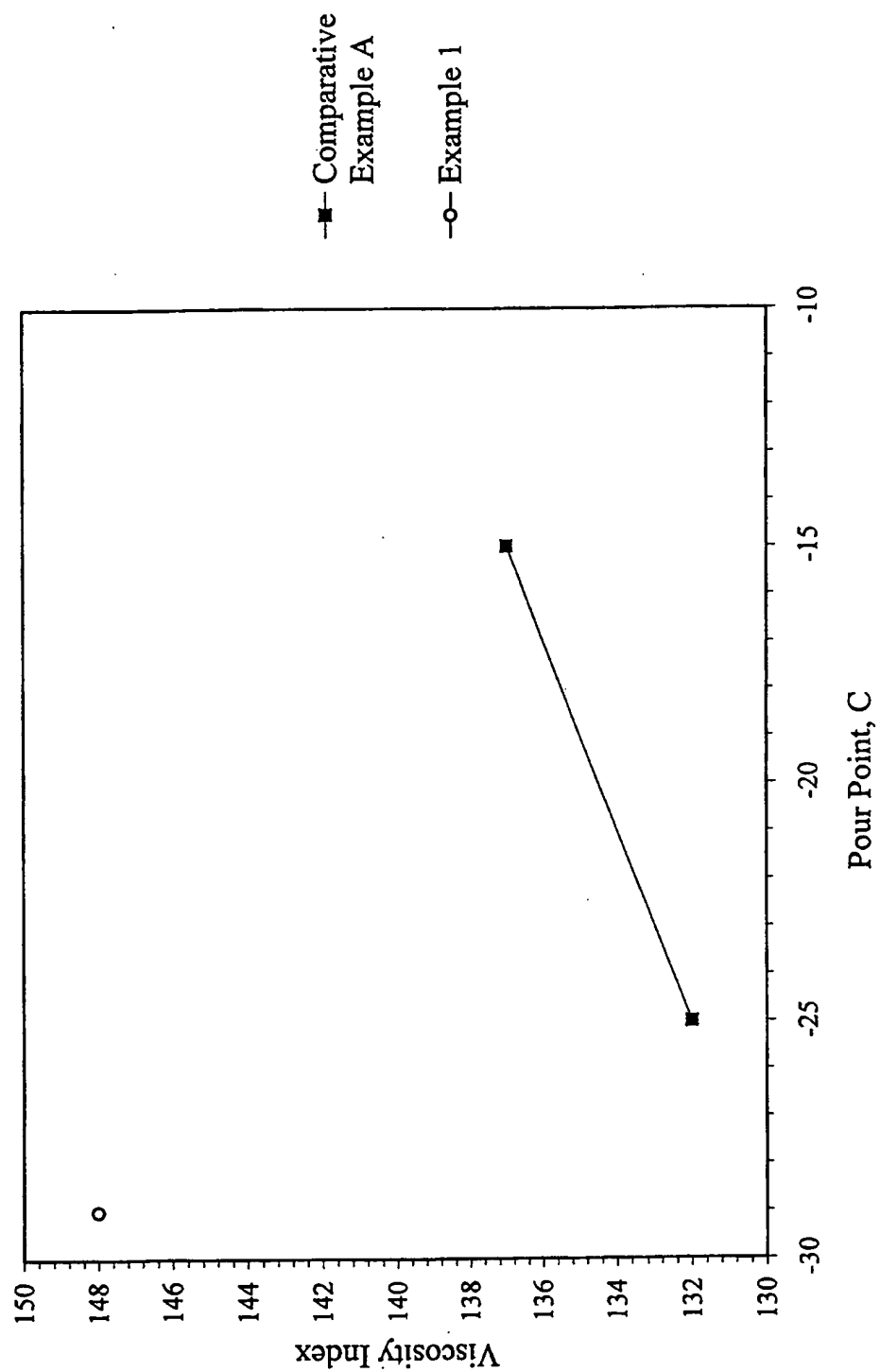
**Figure 2**
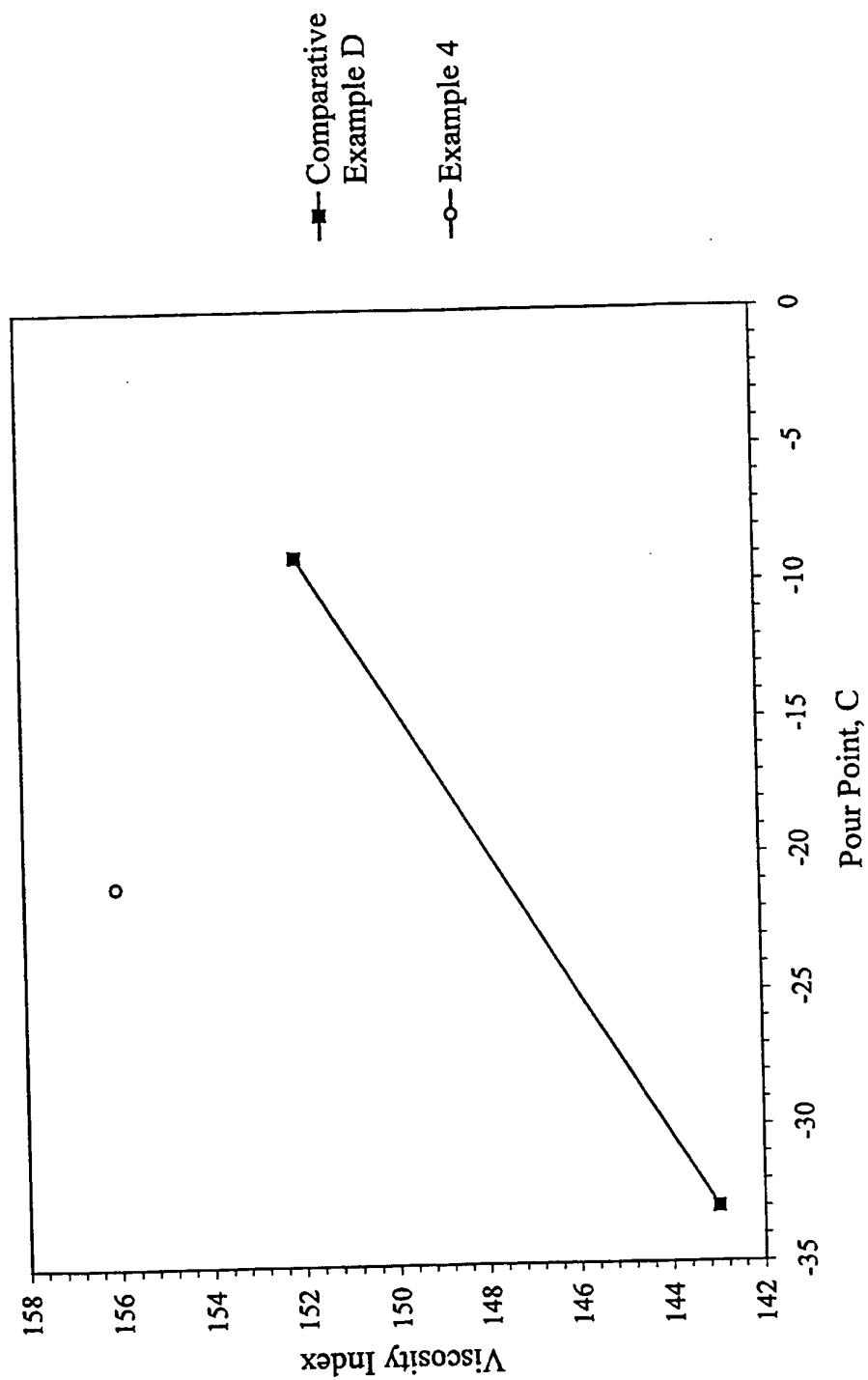
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C10G67/04    C10G45/64

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 4 919 788 A (CHEN NAI Y  ET AL) 24 April 1990<br><br>see claims 1-9 | 1-10, 17-22, 25,26 |
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[X] Further documents are listed in the continuation of box C.      [X] Patent family members are listed in annex.

* Special categories of cited documents :

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 26 April 1999 | 06/05/1999 |

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|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Michiels, P |

# INTERNATIONAL SEARCH REPORT

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

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